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Title : Process for preparing composite membrane to separate CO2 gas

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Priority Information :

Abstract : The patent refers to the field of 'treating gases or vapours: separation, recovering, chemical or biological purification of waste gases'.A composite membrane for separating CO2 gas is made from the hollow or flat membrane of polysulfone, polyacrylonitrile, or polyether sulfone through dipping in polyvinylamine solution for 5-60 min, cross linking with 5-50 % glutaraldehyde solution for 5-40 min and the solution of sulfuric acid or hydrochloric acid for 5-30 min, drying and washing with water. Its advantages lie in easy operation, low cost, and high separating and penetrating power to CO2/CH4.

Claims

1.A kind of CO_2 The composite membrane preparation method of gas delivery, said method is as the basal lamina with the polysulfone, polyacrylonitrile, polyethersulfone hollow membrane or dull and stereotyped film, mainly through steeping in lotion, cross linking, dry, wash the step and prepare CO_2 The composite membrane of gas delivery, characterized by: The lotion uses weight concentration as 0.1-5% polyvinyl amine solution, or space impregnating time as 5-60min continuously; Cross-linking agent uses weight concentration as 5-50% pentanedial solution and sulfuric acid or solution hydrochloride with the concentration of 0.05-1mol/l, crosslinking time are 5-40min and 5-30min each.

2.CO of claim 1 $_2$ The composite membrane preparation method of gas delivery, characterized by: The preferred weight concentration of polyvinyl amine solution is 0.4-2%; The preferred weight concentration of pentanedial solution is 25-50%; The preferred concentration of acid solution is 0.1-0.4mol/l.

CO_2 Composite membrane preparation method of gas delivery

Technical field

The invention belongs to the preparative technique of the composite membrane of gas delivery, say precisely the invention is CO_2 Preparative technique of the composite membrane of gas delivery.

Background art

Anisotropic membrane and compounding the membrane coat to widely apply to method for separating the gas. Though the craft of preparing anisotropic membrane with surface layer of ultrathin zero defect has already been known very well by the insider, preparation method just as United States Patent 4902422 and 4772392 mentioned. However, it is very difficult to prepare of good performance anisotropic membrane, the separating layer of thin surface will usually produce defects such as the crackle, gas pin,etc., and reduce the separating properties of the membrane. The composite membrane adheres to the thin dense surface layer (separating layer) of wrap on the porous basal lamina, the basal lamina can adopt the above-mentioned anisotropic membrane too, usually the separating layer is different from material of the basal lamina, the separating properties of the membrane are decided by separating layer. This characteristic has determined the composite membrane has the advantage that a lot of anisotropic membrane does not possess, such as barotolerancy, resistance to crocking,etc.. In 94110113 China's Patent No., yellow to disclose one intramenbrane to apply vacuum in hollow fibre howabout on the sunny side, dip-coat the method to coat liquid; Cabasso,et al. disclose one form cross-linked polysilicone block coat and cover with one gas divide into at block coat at porous carrier layer in 4702922 United States Patent Make the gas separation membrane method of the multilayer on the abscission layer; Bikson,et al. disclose fiber prepare lipid bilayer, inner ply outside in 5356459 United States Patent; Can see United States Patent 4713292 and 5354469,etc. in other similar examples. The composite membrane prepared at present usually includes three layers: Basal lamina / separating layer / sealant or basal lamina / block coat / separating layer, sealant and block coat have highly elastic siloxane for adoption more, the separating layer of some composite membrane adopts modified siloxane material too.

There are methods such as dip-coating, interfacial polymerization, plasma polymerization and polymerization in situ,etc. to prepare composite membrane. In reality, it was dip coating process that was employed most, said method soaks the basal lamina (hollow fibre or dull and stereotyped membrane) in containing in polymer, prepolymer or monomeric coating, adhere to wrap solution on the basal lamina, then carry on cross linking, and make composite membrane.

Invention content

It is intended that the present invention provides a kind of CO_2 Composite membrane preparation method of gas delivery. Said method is easy to operate, with low costs, the eigen separation and penetrating quality near separating layer material of composite membrane made, and need not prepare sealant or block coat.

The invention is carried out by the following technological schemes: As the basal lamina with the polysulfone, polyacrylonitrile, polyethersulfone hollow membrane or dull and stereotyped film, adopt dip coating process, mainly through steeping in lotion, cross linking, dry, wash the step and prepare CO_2 Composite membrane method of gas delivery. Characterized by that: The lotion uses concentration as 0.1-5% (wt%) polyvinyl amine solution, or space impregnating time as 5-60min continuously; Cross-linking agent uses concentration as 5-50% (wt%) of the pentanedial solution and sulfuric acid or solution hydrochloride with the concentration of 0.05-1mol/ls, crosslinking time are 5-40min and 5-30min each.

The preferred concentration of the above-mentioned polyvinyl amine solution is 0.4-2% (wt%); The preferred concentration of pentanedial solution is 25-50% (wt%); The preferred concentration of acid solution is 0.1-0.4mol/l.

The present inventive process is easy to operate, with low costs, the eigen separation and penetrating quality near separating layer material of composite membrane made, and need not prepare sealant or block coat, the membrane, to CO_2/CH_4 Separation and penetrating quality: $\alpha_{CO2/CH4}>50$,$P_{CO2}>30$GPU.

Specific embodiment

Example 1

Adopt the hollow-fibre membrane of polysulfone as the basal lamina, apply 5 sticks of 20cm long hollow fibre to make into a assembly, the specific operation step is: Fix five sticks of hollow fibre onto fixed tray made by oneself, then, it is in 1% (wt%) polyvinyl amine solution to soak the fixed tray with hollow fibre in the concentration, after impregnating 20min, air dried 10-24 hours in the air; It is in 1% (wt%) polyvinyl amine solution to soak the concentration of the fixed tray again, after impregnating 30min, air dry 10-24 hours in the air; It is in 50% (wt%) pentanedial solution to soak the concentration of the fixed tray, after impregnating 20min, soaked in sulphate solution in a concentration of 0.1mol/l, after impregnating 15min, air dried 10-48 hours in the air; After flushing with water, make CO_2 The composite membrane of gas delivery, carry on the performance test, the membrane, to CO_2/CH_4 Separation and penetrating quality as follows: CO_2 Infiltration rate 4.1 10^{-5} cm^3 (STP)/(cm^2 Sec cmHg), selectivity coefficient $\alpha_{CO2/CH4}=70$.

Comparative example

Adopt the hollow-fibre membrane of polysulfone as the basal lamina, apply 5 sticks of 20cm long hollow fibre to make into a assembly, operate specifically

The step is: Fix five sticks of hollow fibre onto fixed tray made by oneself, then, it is in 1% (wt%) polyvinyl amine solution to soak the fixed tray with hollow fibre in the concentration, after impregnating 20min, air dried 10-24 hours in the air; It is in 1% (wt%) polyvinyl amine solution to soak the concentration of the fixed tray again, after impregnating 30min, air dry 10-24 hours in the air; After flushing with water, make CO_2 The composite membrane of gas delivery, carry on the performance test, the membrane, to CO_2/CH_4 Separation and penetrating quality as follows: CO_2 Infiltration rate 5.2 10^{-5} cm^3 (STP)/(cm^2 Sec cmHg), selectivity coefficient $\alpha_{CO2/CH4}$=35.

Example 2

Adopt the hollow-fibre membrane of polysulfone as the basal lamina, apply 5 sticks of 20cm long hollow fibre to make into a assembly, after specific operation step for fix from hollow fibre of radical onto fixed tray made by oneself suddenly, it is in 0.6% (wt%) polyvinyl amine solution to soak the fixed tray with hollow fibre in the concentration, after impregnating 30min, air dried 10-24 hours in the air; It is in 0.6% (wt%) polyvinyl amine solution to soak the concentration of the fixed tray again, after impregnating 30min, air dry 10-24 hours in the air; It is in 50% (wt%) pentanedial solution to soak the concentration of the fixed tray, after impregnating 10min, soaked in sulphate solution in a concentration of 0.1mol/l, after impregnating 15min, air dried 10-48 hours in the air; After flushing with water, make CO_2 The composite membrane of gas delivery, carry on the performance test, the membrane, to CO_2/CH_4 Separation and penetrating quality as follows: CO_2 Infiltration rate 4.4 10^{-6} cm^3 (STP)/(cm^2 Sec cmHg), selectivity coefficient $\alpha_{CO2/CH4}$=52.

Example 3

Adopt the hollow-fibre membrane of polyacrylonitrile as the basal lamina, apply 5 sticks of 20cm long hollow fibre to make into a assembly, the specific operation step is: Fix five sticks of hollow fibre onto fixed tray made by oneself, then, it is in 1% (wt%) polyvinyl amine solution to soak the fixed tray with hollow fibre in the concentration, after impregnating 20min, air dried 10-24 hours in the air; It is in 0.5% (wt%) polyvinyl amine solution to soak the concentration of the fixed tray again, after impregnating 30min, air dry 10-24 hours in the air; It is in 50% (wt%) pentanedial solution to soak the concentration of the fixed tray, after impregnating 15min, soaked in sulphate solution in a concentration of 0.1mol/l, after impregnating 15min, air dried 10-48 hours in the air; After flushing with water, make CO_2 The composite membrane of gas delivery, carry on the performance test, the membrane, to CO_2/CH_4 Separation and penetrating quality as follows: CO_2 Infiltration rate 4.3 10^{-5} cm^3 (STP)/(cm^2 Sec cmHg), selectivity coefficient $\alpha_{CO2/CH4}$=59.